

COATINGS. ENAMELS

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PREDICTION OF THE EQUILIBRIUM COMPOSITION FOR HIGH-TEMPERATURE REACTION PRODUCTS IN COMPLEX OXIDE SYSTEMS

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Thermodynamic analysis of parallel-serial reaction in complex oxide systems is carried out. The use of the Karapet'yants method to supplement the refined Hooke-Jeeves method has made it possible to determine the optimum range of compositions studied and the most rational temperature interval for heat treatment of coatings. This makes it possible to substantially decrease subsequent experimental search and reduce it to a verification of the optimum interval that is thermodynamically identified.

The possibilities of chemical thermodynamics go beyond establishing the energy possibility of a specific reaction. In particular, a method for calculating an equilibrium phase composition in batch mixtures heat-treated at temperature not less than 1473 K is rarely used. This method makes it possible to predict the qualitative composition of high-temperature reaction products and estimate their quantitative ratios in target material, which is significant for research of crystallizing silicate glasses and substantially speeds up subsequent experimental search; in fact, this search becomes reduced to a verification of the optimum range identified for initial compositions.

A calculation of this kind has been implemented with respect to non-fritted high-temperature glazes, whose structure and properties are formed in the course of melting of an initial batch mixture and become fixed in the cooling of heat-treated articles. The calculation was carried out for compositions with fundamental differences in the content of the main components (Table 1). The mechanism of phase interactions and the properties of coatings based on them will be different as well; therefore, prediction of the equilibrium composition of reaction products is interesting precisely for such oxide systems.

It should be noted that real batch mixtures contain not only individual oxides but also complex natural and chemical compounds (pegmatite, chalk, barium carbonate, waste potassium-iron catalyst, etc.). Identification of their precise

thermodynamic characteristics is problematic; moreover, for such components as the potassium-iron catalyst it is totally impossible. Determination of these parameters based on increments [1] will produce a too big calculation error. In view of this, and also considering that calculations are to be fulfilled for high temperatures (900–1700 K), we believed it more reliable to analyze possible reactions between oxides making up initial materials, which is reflected in the list of reactions proposed. This solution appears even more substantiated considering that some elements of this approach had been validated before [2].

The qualitative and quantitative oxide compositions of non-fritted glazes selected for the study make it possible to

TABLE 1

Oxide	Weight content, %, in glaze						
	3 ₀	3 _{IV}	3 _{VI}	Z ₂₁	Z ₃₃	Z ₃₆	Z ₃₇
SiO ₂	57.8	53.3	56.4	49.3	50.8	48.0	51.2
Al ₂ O ₃	7.6	9.7	7.9	20.0	20.0	18.6	20.0
CaO	16.1	13.2	12.2	3.0	3.5	6.0	4.5
MgO	2.8	2.8	1.6	0.3	0.5	2.2	0.4
BaO	6.2	6.3	6.2	5.5	5.0	6.5	5.0
ZnO	—	—	—	16.0	16.0	14.9	14.5
Na ₂ O	2.1	2.0	2.1	1.9	1.9	1.9	1.9
K ₂ O	2.2	2.0	2.2	1.0	1.0	1.0	1.0
Fe ₂ O ₃	5.2	5.2	5.1	0.3	0.3	0.3	0.3
Cr ₂ O ₃	—	—	—	2.7	1.0	0.6	1.2
TiO ₂	—	5.5	6.3	—	—	—	—

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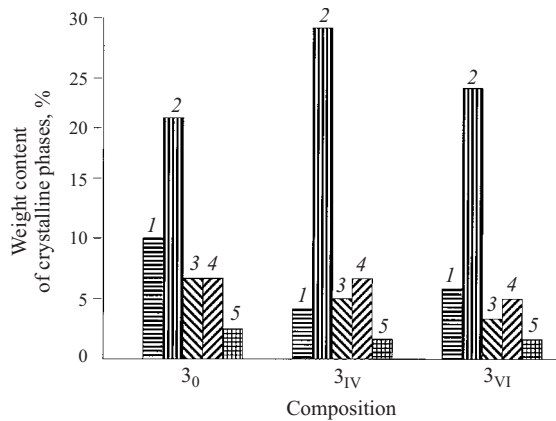


Fig. 1. Equilibrium compositions of products of high-temperature reactions for mixtures of series 3 at 1500 K: 1) diopside; 2) helenite; 3) forsterite, 4) barium ferrite, 5) mullite.

suggest that the most significant processes in batch mixtures will proceed according to the following reactions:

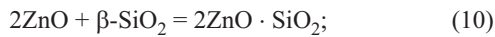
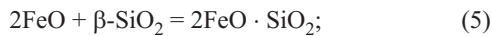
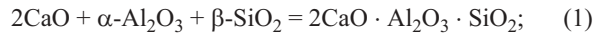


TABLE 2

Reaction	Gibbs energy, kJ, at reaction temperature, K				
	900	1100	1300	1500	1700
1	-124.817	-127.571	-130.195	-132.748	-135.257
2	-82.778	-82.867	-82.881	-82.843	-82.761
3	-10.880	-17.330	-56.867	-68.567	-86.474
4	-17.693	-9.724	+1.485	+15.973	+33.770
5	-11.899	-5.913	-0.140	+5.333	+10.436
6	-52.135	-61.206	-70.675	-80.454	-90.503
7	+3.954	+17.431	+29.785	+40.654	+49.748
8	-57.803	-56.622	-55.706	-55.066	-54.694
9	-14.429	-98.167	-205.154	-333.833	-483.085
10	-18.652	-9.701	+1.207	+13.893	+28.235
11	+10.897	-6.389	-22.481	-37.201	-50.437

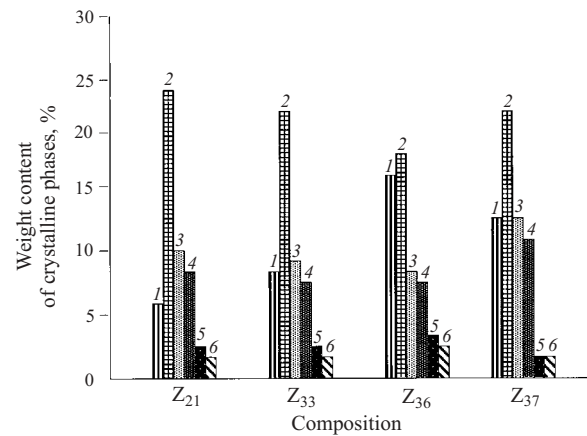
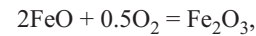


Fig. 2. Equilibrium compositions of products of high-temperature reactions for mixtures of series Z at 1400 K: 1) helenite; 2) mullite; 3) gahnite; 4) sillimanite; 5) magnesium spinel; 6) forsterite.

It should be noted that the oxidation of FeO to Fe₂O₃,



has been left outside the framework of the reactions considered since it is hard to uniquely identify the oxide form of iron in the initial materials. Furthermore, the thermodynamics of this reaction does not have a fundamental effect on the equilibrium composition of the products of phase formation due to subsequent formation of solid solutions with participation of both FeO and Fe₂O₃. Titanium and chromium oxide were not taken into account in the calculation either, since it is known that the former in an amount below 7% (here and elsewhere weight content) predominantly passes into the vitreous phase and the second one due to its high melting point will participate in reactions occurring at temperatures above the considered ones.

The method proposed by Karapet'yants [1] was selected for solving this problem. However, this method is not intended for solving a system of nonlinear high-order equations expected in this problem, therefore, the Hooke – Jeeves method [3] was used in implementation with some necessary refinements [2].

The temperature dependence of the Gibbs energy was preliminary determined for each reaction using the precise integration method [4]. The results obtained with regard to the above considerations are listed in Table 2.

Analyzing the obtained Gibbs energy values, it should be noted that the reaction of formation of hercynite (7) is thermodynamically impossible within the entire temperature interval considered. Furthermore, three other reactions, namely (4), (5), and (10), have a restricted temperature interval of existence.

The HUK-Ceramic program was used to calculate an expected equilibrium composition of the products of the above reactions for each composition with a temperature variation step of 100 K. Based on the calculation data we found that

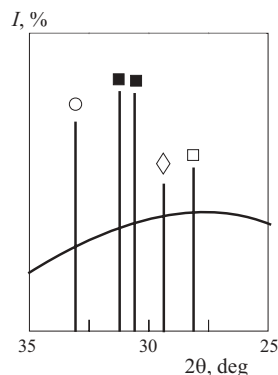


Fig. 3. X-ray diffraction pattern of coating 3_{VI} fired at 1553 K: ○) barium ferrite $BaFe_{0.24}Fe_{0.76}O_{2.88}$; ◇) barium ferrite $BaFe_2O_4$; □) sanidine $KAlSi_3O_8$; ■) diopside $CaMg(SiO_3)_2$.

the main products in series 3 is helenite $2CaO \cdot Al_2O_3 \cdot SiO_2$, whose content within the whole temperature interval is within limits of 20 – 29%. Diopside $CaO \cdot MgO \cdot 2SiO_2$, forsterite $2MgO \cdot SiO_2$, and barium ferrite $BaO \cdot Fe_2O_3$ are also formed in perceptible quantities.

The main reaction product in the composition series Z is $3Al_2O_3 \cdot 2SiO_2$ in an amount up to 25%; its accompanying components are helenite up to 15%, gahnite $ZnO \cdot Al_2O_3$, and sillimanite $Al_2O_3 \cdot SiO_2$.

Figures 1 and 2 show comparative content diagrams of the main crystalline phases in the compositions considered depending on the formation temperature.

The reactions of formation of fayalite $2FeO \cdot SiO_2$, forsterite $2MgO \cdot SiO_2$, and decomposition of magnoferrite $MgO \cdot Fe_2O_3$ occur intensely within a temperature interval of 1000 – 1200 K in batch mixtures 3_0 and 3_{IV} . An opposite situation is registered within the specified interval for compositions 3_{VI} , in which the content of magnoferrite increases insignificantly, and fayalite presumably decomposes, facilitating the formation of barium ferrite.

Phase transformations of fayalite and magnoferrite in all three mixtures end at temperatures of 1200 – 1400 K, whereas the formation of barium ferrite continues and intensifies. Mixtures 3_0 and 3_{IV} are characterized by reactions of diopside with helenite, while the other phases have virtually constant contents. Iron oxide released after the completion of the reactions of formation of fayalite and magnoferrite is consumed to increase the content of $BaO \cdot Fe_2O_3$ and the formation of solid solutions of the type of $(Ba, Fe)Al_2O_4$ or $(Ba, Al)Fe_2O_4$. The formation of color centers responsible for tinting of non-fritted glazes is possible on the basis of the compounds specified above. The series of phase transformations stops within a temperature interval of 1400 – 1600 K and the equilibrium compositions do not change.

Analysis of estimated data for compositions of series 3 suggests that coatings produced at a temperature of 1500 K will have different properties due to the presence of phases having an opposite effect on thermal stability (mullite and

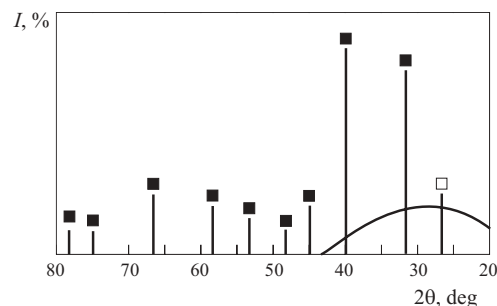


Fig. 4. X-ray diffraction pattern of coating Z_{21} fired at 1523 K: ■) gahnite; □) α -quartz.

forsterite), chemical resistance (diopside and helenite), and color of coatings (iron-bearing solutions).

The calculation of equilibrium compositions for series Z indicates that the formation of willemite in all of them stops at a temperature around 1400 K, which has a substantial effect on the final composition of the reaction products, which exhibits a great variety.

The temperature interval of 1200 – 1500 K exhibits an intense reaction of the formation of zinc spinel. Such abrupt increase in its content in the mixture becomes possible due to the release of ZnO after decomposition of willemite and incorporation of ZnO and SiO_2 into the glass matrix.

Coatings of series Z will resemble each other in their main properties, since they contain a virtually constant quantity of gahnite, which is a compounds imparting high opacity ($n_{av} = 1.82$) and mechanical strength to a finished coating due to its own high hardness (7.5 – 8.0 in the Mohs hardness scale). Furthermore, the capacity of zinc spinel to form solid solutions and its wide isomorphism can be used for the synthesis of colored coatings in the presence of chromium oxide, and color centers based on $ZnO \cdot Al_2O_3$ will be resistant to the effect of aggressive glaze melts.

Thus, by predicting the reaction products in the system considered at the temperatures of the melt formation, the following has been established:

- all phase transformations in composites of series 3 and Z occur at temperatures below 1500 K, which makes it possible to perform heat treatment of coatings at a temperature not higher than the specified one;

- analyzing the final phase composition of heat-treated products, it is necessary to take into account the firing duration of non-fritted glazes (36 – 48 h), due to which such compounds as helenite, sillimanite, and forsterite will most probably pass into the melt, and others, such as gahnite, mullite, and diopside, on the contrary, will be crystallized from the melt;

- with respect to obtaining colored coatings, the most suitable interval is 1400 – 1500 K, since magnesium or zinc spinel most probably are formed within this interval, and favorable conditions are developed for the formation of solid solutions on their basis;

– a color-bearing phase in the optimum coatings of series 3 will presumably be a solid solution of iron, $\text{MgO} \cdot \text{Al}_2\text{O}_3$, and $\text{BaO} \cdot \text{Fe}_2\text{O}_3$, although it is hard to predict the color of coating;

– the optimum coatings of series Z most probably will get their tint from spinelide of complex composition $\text{Zn}(\text{Al}, \text{Cr})_2\text{O}_4$, and the glaze of composition Z_{21} is likely to have the most intense color. Synthesized compositions of non-fritted glazes of the series considered fully corroborated the optimum heat treatment interval found in the calculation, namely, 1503 – 1553 K. High-quality tinted (mustard and inol color) coatings with good luster, thermal resistance, and microhardness were developed due to the synthesis of spinelide compounds.

The phase composition of coatings was determined using x-ray phase analysis (Figs. 3 and 4), which corroborates the calculation validity with respect to both quantitative and qualitative phase content.

Thus, the use of the Karapet'yants method together with the Hooke – Jeeves method and the developed method for setting initial approximations to calculate the system of non-linear equations has made it possible to make a modeling

calculation of equilibrium compositions obtained at various temperatures from various batch mixtures.

A possible mechanism of phase formation for varying temperatures of the system has been identified and the approximate content of reaction products and ensuing properties of the finished coating have been estimated. An optimal heat treatment procedure has been selected to obtain optimum service parameters in coated products.

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